CHAPTER 3

MATERIALS AND METHODS

After a brief literature review, selection of materials and methods has been done since it plays a vital role in the treatment process of wastewater. The raw material used for the preparation of non-conventional adsorbent was *Euphorbia Tirucalli* L wood. Dyes selected for this adsorption study were Acid Orange10, Basic Violet3, Reactive Red and Direct Blue.

3.1 MATERIALS

The low cost adsorbents used in this study were derived from Euphorbia Tirucalli L wood which is economical, abundant and easily available. The precursor wood was collected from local area, cut into pieces of 2 to 3 cm size, dried in sun light for 15 days and used for the preparation of activated carbon. The saw dust of the same wood was modified by coating with polyaniline and polypyrrole. The properties of activated carbon prepared by various process and modified saw dust were also studied as per standard procedures.

3.1.1 Preparation of Adsorbents

a. Carbonization procedures

1. Direct Pyrolysis

   The dried precursor material was carbonized at 400°C and powdered well, then activated at 800°C for 10 minutes. Finally the carbon produced was washed with plenty of water and dried at 110°C (Rengaraj et al 1999).
2. **Carbonisation with H$_2$SO$_4$**

The dried material was treated with excess con. H$_2$SO$_4$. Charring occurred along with evolution of heat. Then the mixture was left in air oven at 140 -160\(^0\)C for a period of 24 hours. Then the product was washed with plenty of water, dried at 110\(^0\)C and activated at 800\(^0\)C for 10 minutes (Guo and Lua 1999, Guo et al 2005 and Rio et al 2005).

3. **Carbonisation with H$_3$PO$_4$**

The dried material was impregnated with 35\% boiling solution of H$_3$PO$_4$ for 2 hours and left for 24 hours, then excess solution decanted off and air dried. The dried material was carbonized at 550\(^0\)C for 1.5 hours in muffle furnace, powdered and activated at 800\(^0\)C for 10 minutes. The resulting carbon was washed with plenty of water to remove the residual acid, dried and powdered (Corcho et al 2006).

4. **Carbonisation with KOH**

The dried material was soaked in 10\% KOH solution and was kept for 24 hours. At the end of this period the excess solution was decanted off and air dried. Then the dried material was carbonized at 400\(^0\)C for 30 minutes, powdered well and was activated in muffle furnace at 800\(^0\)C for 10 minutes. After the activation the carbon was washed with 4N HCl to remove the cations. Then it was washed with plenty of water to remove the acid, dried and powdered (Otowa et al 1997, Yang and Lua 2003 and Wu et al 2005).

5. **Carbonisation with ZnCl$_2$**

The dried material was impregnated with 10\% boiling solution of ZnCl$_2$ for 2 hours and left for 24 hours. Then excess solution was decanted off and air dried. The dried material was carbonized at 400\(^0\)C for 30 minutes in
muffle furnace, was powdered and activated at 800°C for 10 minutes. After the activation the carbon was washed with 4N HCl to remove the cations. Then it was washed with plenty of water to remove the acid, dried and powdered (Tsai et al 1997).

b. **Preparation of Polymer Coated Saw dust Composites**

1. **Polyaniline coated saw dust composite**

   *Euphorbia Tirucalli L* wood saw dust used for the preparation of polymer composite. The saw dust was first washed with distilled water in order to remove impurities and was dried at 60°C for 2 hours. The polymers were synthesized on saw dust surface, which was previously soaked in monomer Aniline solution (0.2 M) for 2 hours at room temperature followed by a slow addition of chemical oxidants 0.2 M Ammonium per sulphate in 1.2 M HCl at room temperature for 4 hours.

   Polymerisation occurred on the surface of saw dust immediately after the addition of the oxidant solution. The polymer coated saw dust were filtered, washed with distilled water and was dried (Ansari and Mosayebzadeh 2010).

2. **Polypyrrole coated saw dust composite**

   The *Euphorbia Tirucalli L* wood saw dust was first washed with distilled water in order to remove impurities and dried at 60°C for 2 hours.
saw dust was filtered, washed with distilled water and was dried (Ansari and Mosayebzadeh 2010).

3.1.2 Adsorbate

Four classes of dyes were selected for the analysis and were obtained from E.Merk, India and were used as received. The structure of dyes studied is presented in Figure 3.1 and some of the properties are given Table 3.2.

Figure 3.1 Structure of the dyes selected for adsorption studies
Table 3.1 List of Adsorbents prepared from *Euphorbia Tirucalli* L wood and their preparation methods

<table>
<thead>
<tr>
<th>S.No</th>
<th>Adsorbents</th>
<th>Preparation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ET1</td>
<td>Pyrolysis Process</td>
</tr>
<tr>
<td></td>
<td>ET2</td>
<td>H$_2$SO$_4$ Process</td>
</tr>
<tr>
<td></td>
<td>ET3</td>
<td>H$_3$PO$_4$ Impregnation</td>
</tr>
<tr>
<td></td>
<td>ET4</td>
<td>KOH Impregnation</td>
</tr>
<tr>
<td></td>
<td>ET5</td>
<td>ZnCl$_2$ Impregnation</td>
</tr>
<tr>
<td>2</td>
<td>PAC</td>
<td>Saw dust coated with polyaniline</td>
</tr>
<tr>
<td></td>
<td>PPC</td>
<td>Saw dust coated with polypyrrole</td>
</tr>
</tbody>
</table>

Table 3.2 Details of dyes selected for the adsorption studies

<table>
<thead>
<tr>
<th>S.No</th>
<th>Dye</th>
<th>Mol. Formula</th>
<th>Mol.Wt</th>
<th>$\lambda_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acid Orange 10</td>
<td>C$<em>{16}$H$</em>{10}$O$_7$N$_2$S$_2$Na$_2$</td>
<td>452.38</td>
<td>478 nm</td>
</tr>
<tr>
<td>2</td>
<td>Reactive Red</td>
<td>C$<em>{31}$H$</em>{13}$ClN$<em>7$O$</em>{10}$S$_6$Na$_5$</td>
<td>1136.31</td>
<td>543 nm</td>
</tr>
<tr>
<td>3</td>
<td>Direct Blue</td>
<td>C$<em>{34}$H$</em>{24}$N$_6$Na$<em>4$O$</em>{16}$S$_4$</td>
<td>992.8</td>
<td>608 nm</td>
</tr>
<tr>
<td>4</td>
<td>Basic Violet 3</td>
<td>C$<em>{25}$H$</em>{30}$ClN$_3$</td>
<td>407.97</td>
<td>540 nm</td>
</tr>
</tbody>
</table>

3.2 METHODS

3.2.1 Characterisation Studies

3.2.1.1 pH and conductivity

Ten gram of carbon in 200mL of distilled water was equilibrated by agitating at 200 rpm for 1 hour. The supernatant solution was analysed for pH and conductivity using Elico pH meter (model) and conductivity meter (model) respectively (ISI, 1977).
3.2.1.2 Moisture content

Five gram of the carbon was weighed accurately in a petridish. The dish was placed in an electric oven maintained at 110 ± 5°C for 5 hours. The dish was covered, cooled in a desiccator and then weighed. Heating, cooling and weighing was repeated at 30 minutes intervals until the difference between the two consecutive weighing was less than 5 mg (ISI 1977).

\[
\text{Moisture content (\%)} = \frac{(M_a - X)}{M_a} \times 100 \quad (3.1)
\]

where, \( M_a \) – Weight of adsorbent taken for test (g)
\( X \) – Weight of adsorbent taken after drying (g)

3.2.1.3 Volatile Matter

One gram of moisture free carbon was weighed accurately in a silica crucible. The crucible was covered, heated in a muffle furnace at 900 ± 20°C for 7 minutes. After heating, the crucible was cooled in a desiccator and then weighed. Heating, cooling and weighing was repeated at 30 minutes intervals until the difference between the two consecutive weights was less than 1 mg (ISI 1977).

\[
\text{Volatile matter percent by weight (\%)} = \frac{(M_a - Y)}{M_a} \times 100 \quad (3.2)
\]

where, \( M_a \) – Weight of moisture free adsorbent taken for test (g)
\( Y \) – Final weight of the adsorbent (g)

3.2.1.4 Ash content

One gram of moisture free carbon was weighed accurately in a tarred porcelain crucible. The crucible was ignited in an electric muffle
furnace at a temperature of 800ºC for 2 hours, and was cooled and weighed. The process of heating and cooling was repeated until the difference between two consecutive weighing was less than 1 mg (ISI 1977).

\[
\text{Ash (on dry basis) percent by weight (\%) = } \frac{M_1}{M_2} \times 100 \tag{3.3}
\]

where, \( M_1 \) – Weight of ash (g)  
\( M_2 \) – Weight of moisture free adsorbent taken for the test (g)

Ash (on dry basis) percent by weight

**3.2.1.5 Matter soluble in water**

Five gram of the moisture free carbon was weighed accurately and transferred into a 1 litre beaker. About 100 mL of distilled water was added and heated to boiling with continuous stirring. Stirring was continued for 5 minutes after the flame was removed. The material was then allowed to settle. The supernatant was filtered through a gouch crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker by using 100 mL of water each time. The combined filtrate was evaporated to almost dryness on a boiling water bath and finally dried in an electric oven, maintained at 100 ± 5ºC cooled in a desicator and weighed. The procedure of drying and weighing was repeated at 30 minutes intervals, until the difference between the consecutive weights was less than 5 mg (ISI 1977).

\[
\text{Matter Soluble in Water (\%) = } \frac{M_1}{M_2} \times 100 \tag{3.4}
\]

where, \( M_1 \) – Mass of the residue (g)  
\( M_2 \) – Weight of the moisture free adsorbent taken for test (g)
### 3.2.1.6 Matter soluble in acid

Five grams of the moisture free carbon was weighed accurately and transferred into a 1 litre beaker. About 100 mL of 0.25 N HCl was added and heated to boiling with continuous stirring. Stirring was continued for 5 minutes after the flame was removed. The material was then allowed to settle. The supernatant was filtered through a gouch crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker using 100 mL of acid each time. The combined filtrate was evaporated to almost dryness on a boiling water bath and finally dried in an electric oven, maintained at 100 ± 5°C cooled in a desicator and weighed. The procedure of drying and weighing was repeated at 30 minutes intervals, until the difference between the consecutive weights was less than 5 mg (ISI 1977).

\[
\text{Acid Soluble matter (\%) = } \frac{A}{M} \times 100
\]  

where,  

\( A \) – Mass of the dried residue (g) 

\( M \) - Weight of the moisture free adsorbent taken for test (g)

### 3.2.1.7 Bulk Density

For the determination of bulk density, a 50 mL graduated cylinder was weighed and a trip balance was used to fill the carbon in the cylinder. Sufficient amount of the carbon was poured with constant tapping and filled to the 50 mL mark. The shaker attached to the balance was adjusted, so that the carbon fills the graduated cylinder at approximately 1 mL per second. After filling the graduated cylinder with carbon, it was weighed accurately. The bulk density was calculated by dividing the weight of carbon by 50 (ISI 1977).
3.2.1.8 Specific Gravity

Five gram of oven-dried carbon sample was placed in a small porcelain dish with 50 mL of distilled water and the contents were heated to boiling gently for 3 minutes to expel the air. After cooling in a water bath to 25 ºC the carbon suspension was transferred to a 100 mL pyconometer with the help of a small funnel, a wire and a wash bottle. The pyconometer was filled with water and stoppered carefully, not to leave any air bubbles in the container. The pyconometer was dried with a piece of cloth and weighed (Wilde et al 1992).

\[
\text{Specific gravity} = \frac{\text{Weight of Adsorbent (Wa)}}{\text{Volume of displaced water (V)}}
\]  \hspace{1cm} (3.6)

where,

\[
V = \frac{(Wa + Wb + Wc)}{\text{Density of water}}
\]  \hspace{1cm} (3.7)

\begin{align*}
W_b & \quad \text{Weight of pyconometer with water (g)} \\
W_c & \quad \text{Weight of pyconometer with adsorbent suspension (g)}
\end{align*}

3.2.1.9 Porosity

Porosity was determined from the specific gravity (S) and bulk density (D) values of carbon (ISI 1977) by applying the following formula

\[
\text{Porosity}(\%) = \frac{(S - D)}{S} \times 100
\]  \hspace{1cm} (3.8)

3.2.1.10 Methylene blue number

Adsorption test of methylene blue on activated carbon was studied by placing 1 gm of carbon in 250 mL beaker. Methylene blue stock solution was added from the burette, with constant stirring. The residual colour of the
solution was observed. The end point was reached if any blue colour remains. Methylene blue number was thus calculated in mg/g (Mental 1968).

3.2.1.11 Iodine Number

About 100 mg of the carbon and 50 mL of 0.025 M iodine solution was mixed and stirred at 150 rpm for 1 hour at 30°C. During the process, iodine was adsorbed by the carbon. The supernatant was titrated with 0.1 N sodium thio sulphate solutions with vigorous stirring. The iodine adsorbed by the carbon (mg/g) was estimated from the difference between the initial and final iodine concentration (Cooney 1998).

3.2.1.12 Surface area and SEM studies

The BET surface area (Brunauer et al 1938) of all activated carbon samples were measured at 77 K using N₂ gas sorption analyzer (Nova 1000, Quanta Chrome Corporation, USA). In order to determine the pore characteristics for the selected carbon (ET3) the N₂ adsorption-desorption isotherms were studied using ASAP 2020 Gas sorption analyzer. The morphological characteristics of the activated carbon samples and polymer coated saw dust composites were studied using JSM-5610LV (JEOL-JAPAN) Scanning Electron Microscope (SEM).

3.2.2 Batch Desorption Studies

After washing the dye loaded carbon with double distilled water, 500 mg of carbon was agitated with 50 mL of distilled water of various pH above the equilibrium time.

3.2.3 Application Studies Using Industrial Effluents

Industrial effluents containing dyes from textile dyeing industries were collected from such industries located near Erode, India. The wastewater
samples were collected from the outlets before discharging the effluent into common collection tank. The characteristics of sample effluents pH, conductivity, Total Dissolved Solids, Colour, Optical Density, Alkalinity, Hardness, Chlorides, Sulphates, Chemical Oxygen Demand and Biological Oxygen Demand were analysed as per the standard procedures (ISI 1977, APHA 1980, Mendham et al 2003). Then 100 mL of the effluent was agitated with varying quantity of adsorbents ET3, PAC, PPC and commercial charcoal for 120 minutes. The supernatant was separated and analysed as before.

3.2.4 Adsorption Kinetic Study

A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for the efficiency of the process. The study of adsorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of adsorbate uptake at the solid-solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transfer process (Metcalf and Eddy 2003).

The model of adsorption kinetics were correlated with the solution uptake rate, hence these models are important in water treatment process design. The rate of kinetics of dye adsorption on ET3 and polymer coated saw dust composites were analysed using pseudo-first order (Lagerygren 1898), Pseudo-second order (Ho and McKay 1999) and intraparticle diffusion models (Weber and Morris 1963).

3.2.4.1 Pseudo-first order kinetics

The pseudo-first order model assumes that the rate of change of solute uptake with time is directly proportional to the difference in amount at saturation and amount of solute adsorbed.
Pseudo-first order Lagergren kinetic equation can be expressed as follows:

\[
\frac{dq}{dt} = k_1(q_e - q_t)
\]  

(3.9)

The integrated form of equation

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}
\]  

(3.10)

where, \(q_e\) is the amount of dye adsorbed at equilibrium (mg/g), and \(q_t\) is the amount of dye adsorbed at time ‘t’ (mg/g), \(k_1\) is the first order rate constant (min\(^{-1}\)) and ‘t’ is time (min). A linear trace was expected between the two parameters “ \(\log(q_e - q_t)\)” and “t”, provided the adsorption follows first order kinetics. The values of \(k_1\) and \(q_e\) can be calculated from intercept and slope of the plot \(\log (q_e - q_t)\) vs time.

### 3.2.4.2 Pseudo-second order kinetics

The Pseudo-Second Order model was then used for the analysis of adsorption kinetics. The pseudo-second order model is based on the assumption that the rate-limiting step may be chemical sorption or chemical sorption involving valance forces through sharing or exchange of electrons between sorbent and sorbate. It was assumed that the adsorption capacity is proportional to the number of active sites occupied on the sorbent.

The dye adsorption described by a modified second order equation is expressed as

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]  

(3.11)
where, $k_2$ is the rate constant of pseudo-second order adsorption (g/mg/min).

The initial adsorption rate, $h$ (mg/g/min), as $t \to 0$ can be defined as

$$h = k_2 q_e^2 \quad (3.12)$$

If the adsorption follows pseudo-second order kinetics, a plot of "$t/q_e$" and "$t$" should give a linear relationship. The values of second order rate constant $k_2$ and $q_e$ were calculated from the intercepts and slopes of the plot.

### 3.2.4.3 Intra particle diffusion model

It is important to determine the rate determining step in adsorption studies. Since the particles are vigorously agitated during the experiment, there is a possibility that transport of adsorbate ion from the solution into the pores of adsorbent is the rate limiting step. The pseudo-first order and pseudo-second order kinetic models could not identify the diffusion mechanism. Then the kinetic results were then analysed by using the intra particle diffusion model to elucidate the diffusion mechanism. The intra particle diffusion model is expressed as

$$t^{1/2} = k_{id} + C \quad (3.13)$$

The possibility of intra particle diffusion was tested by plotting a graph between the amount of dye adsorbed and $t^{1/2}$ at different time intervals.

### 3.2.5 Adsorption Isotherm

The adsorption isotherms are basic requirements for the design of adsorption systems. Adsorption isotherm is basically important to describe how solutes interact with adsorbents and is critical in optimizing the use of adsorbents.
The relationship between adsorbed dye concentration and concentration of the solution at equilibrium is described by isotherm models of which Langmuir and Freundlich are the most widely used isotherm models.

### 3.2.5.1 Langmuir Model

The Langmuir model (1918) is based on the assumption that each active site can only hold one adsorbate molecule. The linear equation given by the Langmuir isotherm is expressed as

\[
\frac{C_e}{q_e} = \frac{1}{Q_0 b_L} + \frac{C_e}{Q_0}
\]

(3.14)

where, \(C_e\) is the equilibrium concentration (mg/L), \(q_e\) is the amount of dye adsorbed at equilibrium (mg/g) and \(Q_0\) (mg/g) and \(b_L\) (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The values of \(Q_0\) and \(b_L\) calculated from the slopes and intercepts of the linear plots of \(Ce/qe\) vs \(Ce\).

The dimensionless parameter of the equilibrium or separation factor or the equilibrium parameter or the adsorption intensity based on Langmuir isotherm can be expressed by the following equation (Hall et al 1966).

\[
R_L = \frac{1}{(1 + bC_0)}
\]

(3.15)

The \(R_L\) value indicated the type of adsorption isotherm to be either unfavourable (\(R_L > 1\)), favourable (\(R_L < 1\)), linear (\(R_L = 1\)) or irreversible (\(R_L = 0\)).
3.2.5.2 Freundlich Model

The Freundlich model is employed to describe the heterogeneous system, which is characterized by heterogeneity factor 1/n. It considers multilayer adsorption with heterogeneous energetic distribution of active sites accompanied by interactions between adsorbed molecules. The Freundlich isotherm is expressed as

\[
\log q_e = \log K_f + \frac{1}{n} \log c_e.
\] (3.16)

where, \(k_f\) and \(n\) are Freundlich constants related to the measure of adsorption capacity and \(n\) is adsorption intensity respectively. These parameters are calculated from intercept and slope of a linear plot of \(\log q_e\) versus \(\log C_e\). The experimental Freundlich model is known to be satisfactory for low concentrations and based on sorption on a heterogeneous surface.

3.2.6 Adsorption Thermodynamics

In order to determine the temperature dependence of the dye removal process by adsorbent, the change in the thermodynamic parameters free energy change (\(\Delta G^0\)), enthalpy change (\(\Delta H^0\)) and entropy change (\(\Delta S^0\)) were analyzed by using VantHoff equation

\[
\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}
\] (3.17)

\[
\Delta G^0 = \Delta H^0 - T\Delta S^0
\] (3.18)

where, \(T\) is the absolute temperature and \(K_L\) (L/g) is the standard thermodynamic equilibrium constant. By plotting a graph of \(\ln K_L\) vs \(1/T\), the values of \(\Delta S^0\) and \(\Delta H^0\) can be estimated from the slope and intercept.
3.2.7 Activation Energy

The second order rate constant of the dye adsorption is expressed as a function of temperature by Arrhenius relationship (Singh and Srivastava, 1999).

\[
\ln k_2 = \ln A - \frac{E_a}{RT}
\]  

(3.19)

where \(E_a\) and \(A\) refers to Arrhenius activation energy and Arrhenius factor obtained from the slope and intercepts of a graph by plotting \(\ln k_2\) vs \(1/T\). The value of activation energy gives an idea about the nature of adsorption process.